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This progress report covers the second Quarter of Phase 2 for the period from September 1, 2006 through November 30, 2006, of the above Thin Film Photovoltaic Partnership Program subcontract.

In this quarterly report we will focus on the research related to the location of copper used as part of the back contact processing in our sputtered CdTe cells. We describe a series of experiments involving peel-off of the back contact and then recontacting again while several measurements were made along the way with x-ray fluorescence to monitor the Cu signal and other measurements were made with high resolution SEM and TEM. Finally, x-ray fine structure measurements provide information on the bonding of Cu in the finished cells. All three measurements together provide evidence that Cu remains localized predominantly very near the back contact in the UT sputtered cells with evaporated Cu/Au back contacts.

1. Recontacting Experiments and Dependence on Cu Thickness

Previous EXAFS studies of fused silica/CdS/CdTe/Cu/Au structures prepared at UT provided evidence of the nearest neighbors of Cu in our sputtered cells and showed that the majority of Cu used for the back contact activation stays at the CdTe/back-contact (BC) or possibly resides along grain boundaries. The objective of those studies was to explore the chemical state of Cu in a structure which is as close to the real cell as possible.

The only difference between the structures studied and a typical working UT cell was the substrate used. Instead of using TCO-coated glass, a pure quartz substrate was used. This way we had extra assurance that there would be no residual elements in the substrate and therefore no undesired background obscuring the Cu signal. For the same reason we avoided using a ZnO coating especially taking into account the proximity of Cu K-alpha and Zn K-alpha edges.

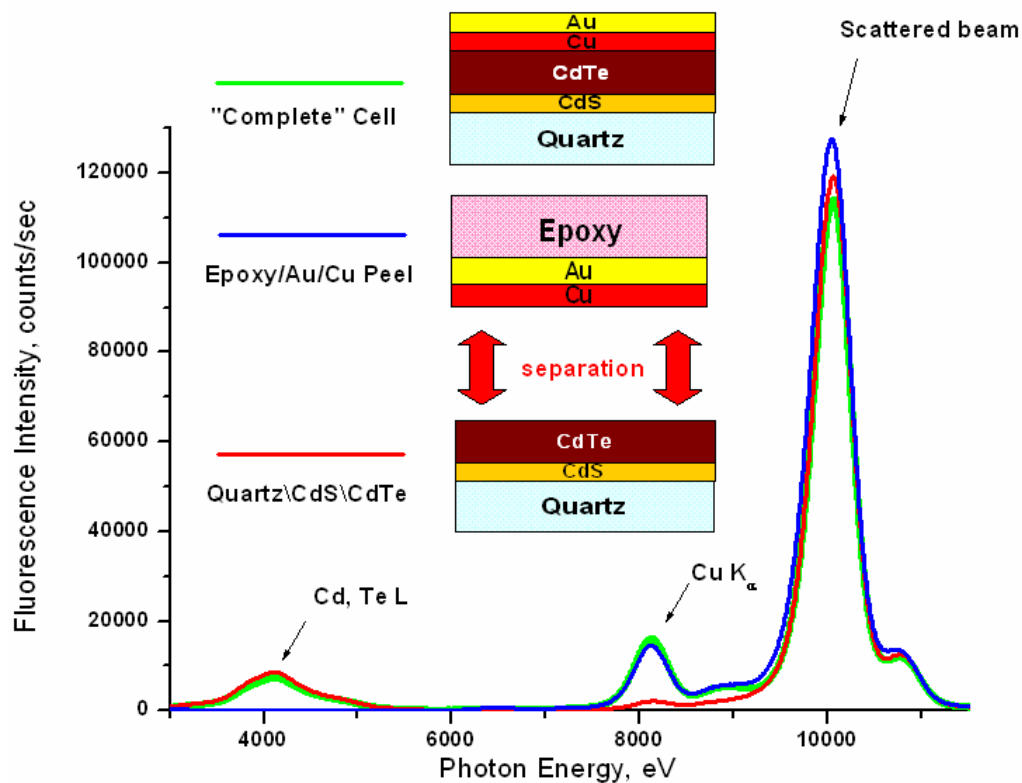


Figure 1. A sketch of the “peel-off” procedure and corresponding X-ray fluorescence spectra of the complete cell, Quartz/CdS/CdTe part and the back contact peel.

Furthermore, we wanted to remove the upper Au layer to prevent undesired distortion in data extraction because of signal attenuation. This led us to a “peel-off” sample preparation technique which can be described as follows:

1. Standard ultrasonic cleaning of 1mm quartz substrate using Micro-90 soap solution
2. Deposition of 0.13 micron CdS by magnetron sputtering
3. Deposition of 2.3 micron CdTe by magnetron sputtering

4. 30 minutes CdCl_2 treatment at 387°C
5. 30\AA Cu/ 200\AA Au back contact deposition by thermal evaporation
6. 45 minutes Cu “activation” treatment in air at 150°C to facilitate Cu diffusion at the back contact
7. Application of LOCTITE R, Quick SETtm Epoxy over the cell area
8. Full cure of the epoxy
9. Heating up the sample for 2 minutes to about 50°C
10. Peeling off the epoxy layer with Au back contact film adhered to it using tweezers

It was found that careful removal of the epoxy with the back contact layer does not damage the underlying structure and in many cases a new back contact can be redeposited on the top of it to form a working cell.

The “peel-off” technique describe above allowed us to compare the Cu x-ray fluorescence spectra of the full Quartz/CdS/CdTe/Cu/Au with the spectra of the parts separated after peeling, *viz*, Quartz/Cds/CdTe and the peeled-off metal layers. The results along with the sketch of the peeled off structure is illustrated in . Fluorescence was excited by a monochromatic x-ray beam of the Argonne APS synchrotron with energy of 10 keV. Elastic scattering of the incident beam is responsible for the most intense peak shown in with that energy. The two other denoted peaks are the 8.1 keV Cu K-alpha and closely spaced Cd and Te L-alpha and L-beta peaks that appear to be one a single broad one at the energy about 4.2 keV. It is remarkable that while the spectrum of the complete structure exhibits both Cu and Cd/Te fluorescence peaks, after the separation the peeled-off contact has very little Cd or Te and the qtz/CdS/CdTe has very little Cu.

Next two figures address this in more detail. In Figure 2 there is a magnified peak of the Cd and Te L fluorescence. Note that this peak only appears in the spectra of the complete structure and Quartz/CdS/CdTe sample. The lower intensity of the Cd/Te peak of the complete structure is likely due to attenuation by the overlying Au layer. The spectrum of the delaminated metal layer on the other hand does not have a detectable peak of these heavy elements which indicates that peeling occurs very cleanly and abruptly at CdTe / back contact interface.

The situation with Cu K-alpha peak illustrated in Figure 3 is completely opposite. The peak in the spectrum of the complete cell appears to be a superposition of the peaks of the other two. A quantitative estimation suggests that the intensity of the Cu peak from the Quartz/CdS/CdTe part of the cell is roughly 10 times less intense than from the peeled off part of it. This suggests that during a standard UT cell fabrication process the majority of the copper (about 90%) remains on the CdTe/BC contact interface even after the thermal diffusion/activation treatment at 150°C for 45 minutes in air. Our EXAFS studies have shown that this Cu is primarily in the form of oxides, while other 10% is likely to be diffused into the structure, including along the grain boundaries, and cannot be removed by physical separation along the interface as in case of interfacial oxide layer removal during the “peel-off” process.

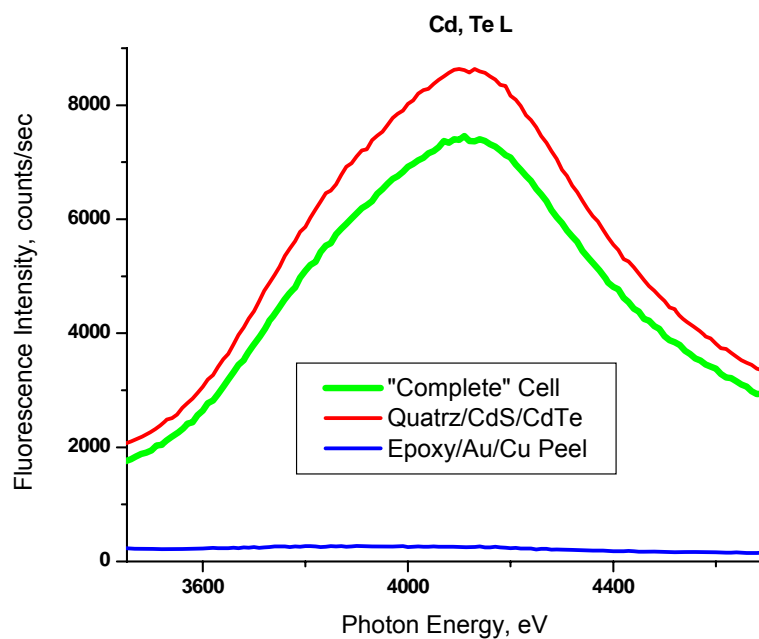


Figure 2. Fluorescence from Cd and Te on the spectra of the complete cell and Quartz/CdS/CdTe sample and its absence on the back contact peel spectrum.

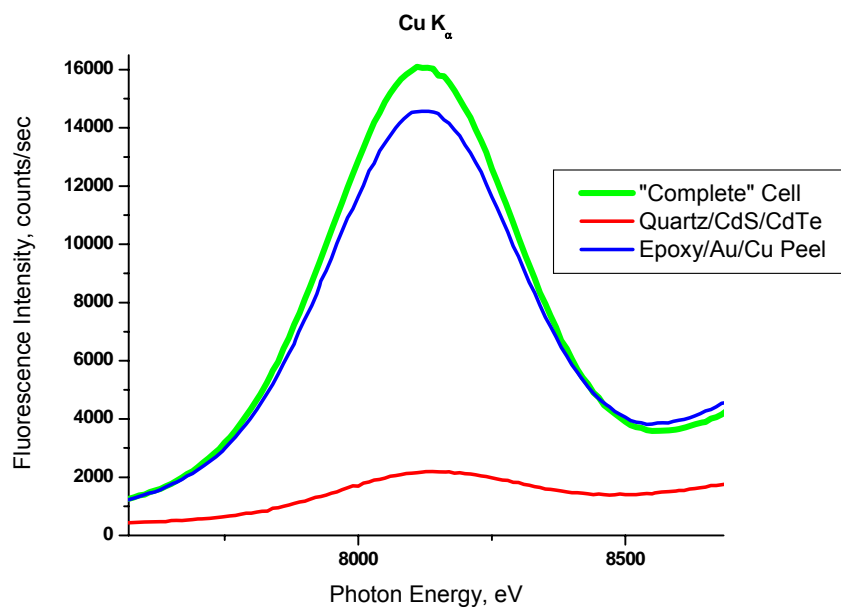


Figure 3. Cu K-alpha fluorescence signal from the 3 structures.

This result suggests that Cu in CdS/CdTe cells exists in two different forms both of which can potentially contribute both to enhanced cell performance and to Cu-associated cell degradation.

It has been suggested that although Cu diffusion is a necessary step to achieve good cell performance, minimizing its amount may have a positive effect on device long-term stability. Therefore we designed an experiment to obtain statistically significant sets of data on how the amount of as-deposited Cu affects cell efficiency. The experiment illustrated in Figure 4 was designed for that purpose.

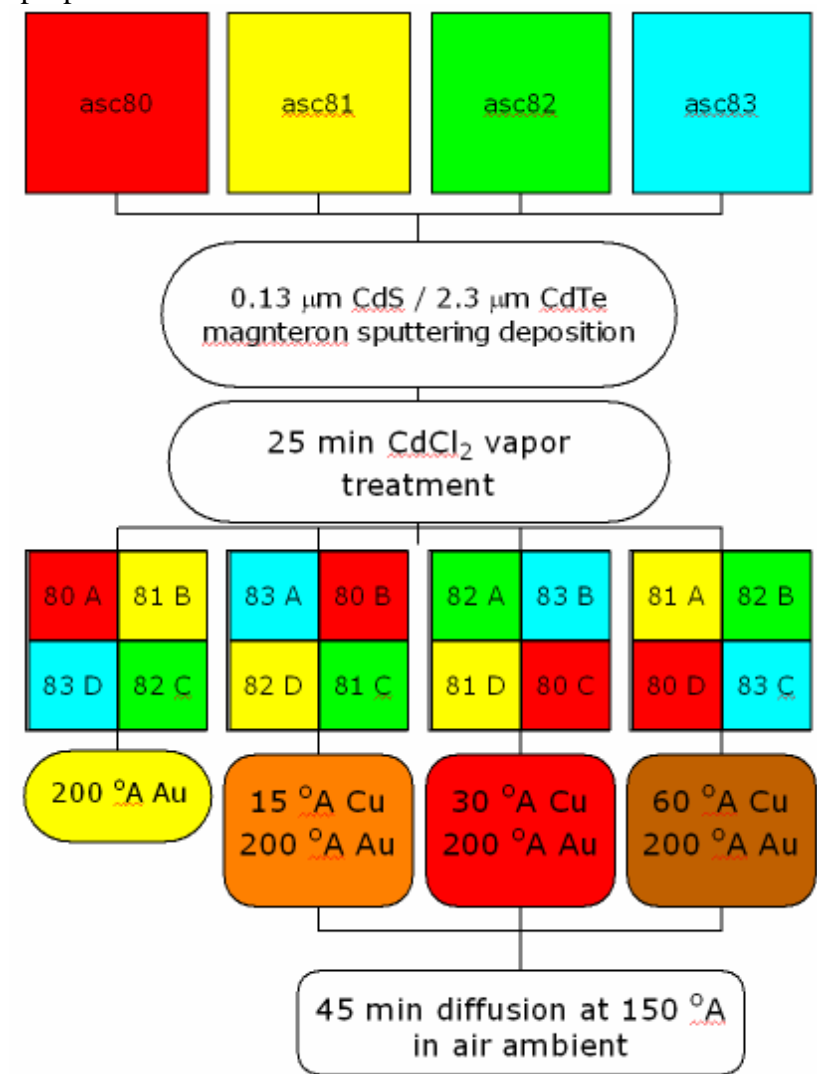


Figure 4. Flowchart of the experiment designed for study of the effect of as-deposited Cu layer thickness on cell performance

Four nominally identical 3"×3" plates of 0.13 micron CdS / 2.3 micron CdTe were deposited on TEC-7 substrates and CdCl₂ treated afterwards using standard UT processing parameters. Right before the back contact application each sample was cut into 4 parts to create 16 separate pieces that were combined together as shown on the experiment diagram. As a result, four batches of samples were made with each batch containing a piece from each of four 3"×3"

samples. A specific different back contact scheme was applied to each batch such that as a result we had:

- 4 pieces with 200Å Au contact, no thermal activation
- 4 pieces with 15 Å Cu / 200Å Au contact, 45 minutes of thermal activation at 150°C in air ambient
- 4 pieces with 30Å Cu / 200Å Au contact, 45 minutes of thermal activation at 150°C in air ambient
- 4 pieces with 60Å Cu / 200Å Au contact, 45 minutes of thermal activation at 150°C in air ambient

Each quarter piece of a plate contained 16 cells with the contact area of 0.1 cm². The efficiency of each cell was measured and is provided in Figure 5 with the four separate groups divided according to the back contact scheme and each group containing about 60 individual cells.

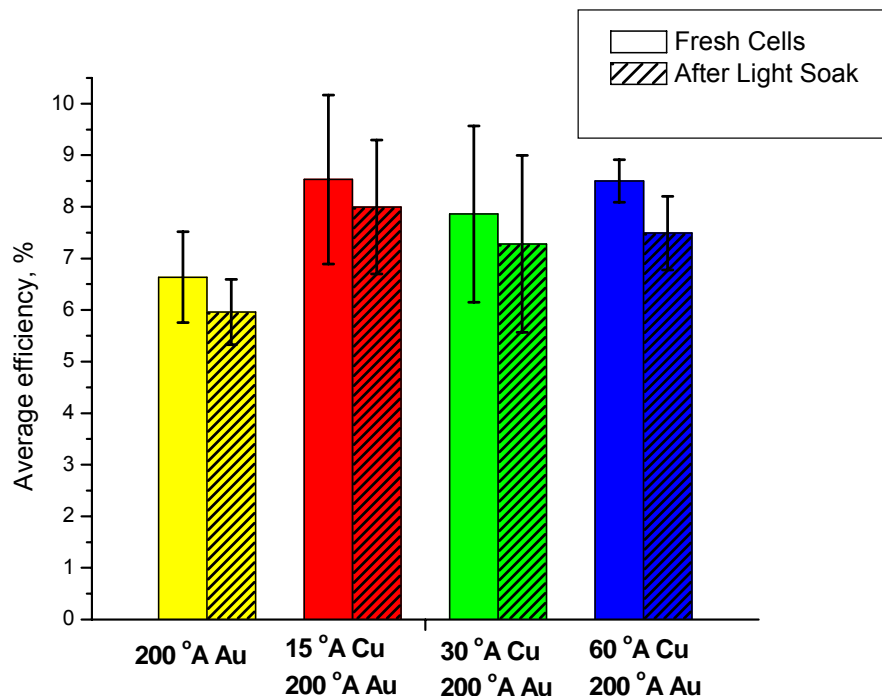


Figure 5. Average efficiency vs. as-deposited Cu layer thickness, before and after light soaking.

It can be seen from Figure 5 that while the difference between no-Cu and Cu-diffused cell is obvious, the amount of Cu between 15 and 60 Å does not have a strong correlation with cell efficiency. This can be attributed to the fact that if copper acts as a p-type dopant after it is diffused into the bulk of CdTe it does not really matter how thick the as-deposited layer of Cu is. Taking into account the results described on page 2 that only about 10% of 35Å thick Cu

diffuses into the bulk, 15Å and 60Å as-deposited Cu layers effectively act as infinite source of diffusion that provide a similar diffusion profile in each case.

The same cells were measured after 10-day (240 hours) light soak at 1 sun (AM 1.5) intensity. For each group degradation was observed although there was not strong correlation with the thicknesses of Cu layers.

The next step was to fabricate a cell that would not have any interfacial Cu, but at the same time had a p-type back contact region formed as a result of Cu diffusion. To achieve this goal we implemented the same “peel-off” technique described previously followed by the deposition of a new back contact on top of the area from there the old one was peeled off.

We started from TEC-7/0.13 micron CdS/2.3 micron CdTe/30Å Cu/200Å Au structures that were CdCl₂ treated. The efficiency of these cells was measured twice and saved and the data were used for comparison later on. The first measurement was before Cu thermal activation, and the second time after diffusion was completed. In addition a set of samples with TEC-7/0.13 micron CdS/2.3 micron CdTe/200Å Au (i.e. without Cu) was made. These cells were also measured, but kept intact afterwards.

Therefore at the end of the first stage of this “recontact” experiment we had J-V data for the following sets of cells:

- a) Tec-7/0.13 micron CdS/2.3 micron CdTe/30Å Cu/200Å Au without Cu diffusion
- b) Tec-7/0.13 micron CdS/2.3 micron CdTe/30Å Cu/200Å Au after Cu diffusion
- c) Tec-7/0.13 micron CdS/2.3 micron CdTe/200Å Au (no heat treatment after back contact deposition)

After the second J-V characterization, the back contacts of Cu-containing cells were lifted off and another back contact was redeposited on top of the original contact areas using a carefully aligned mask with dots of slightly smaller size. The secondary back contact schemes were applied as:

- d) 30Å Cu/ 200Å Au “recontact” without second diffusion;
- e) 30Å Cu/ 200Å Au “recontact” after second diffusion; and
- f) 200Å Au “recontact” without secondary heat treatment.

Finally we had six different categories of cells with different back contact schemes to compare and analyze with the main question to ask - “do we need to have an interfacial layer of Cu/Cu₂O that contains about 90% of the total amount of Cu in the cell? Or can it be removed without a significant drop of cell performance?”. Figure 6 and the discussion after answer this question.

- a) The thin red line of Figure 6 is a J-V characteristic of a typical UT cell and should be considered an “reference” one in this case. All other curves should be compared to it, which is relatively easy in three of five other cases illustrated on Figure 6.
- b) The thin blue line corresponds to the cell with pure gold back contact. It shows an often seen J-V curve with low V_{oc} and vicious rollover indicating a large back barrier.
- c) The thin green line is for a Cu/Au back contact without thermal activation treatment. The V_{oc} is slightly higher than in the previous case and the rollover is a little less dramatic. However, it is a poor cell overall.
- d) The thick green line is the first of the “recontacted” cells – a Cu/Au recontact *without diffusion*. In general it is similar to the previous case and needs some more explanation considering the next situation.

- e) The thick red line is a Cu/Au “recontact” *after diffusion*. It shows a substantial increase of device performance over the previous case. It is not as good as the “reference” cell due to a poorer J_{sc} , but the V_{oc} is just as high and there is no obvious back barrier indication. At the same time this cell contains even more Cu than the standard cell does, but secondary diffusion did not lead to increase of the performance as compared to the “reference” cell.
- f) The thick blue line is the last and the most interesting case – a pure Au recontact. Its J-V curve is almost identical to the previous case and still inferior to the “reference” again due to the loss of J_{sc} . On the other hand this cell contains about 10% of the amount of Cu that UT reference cell does. We are in the process of comparing the long term stability.

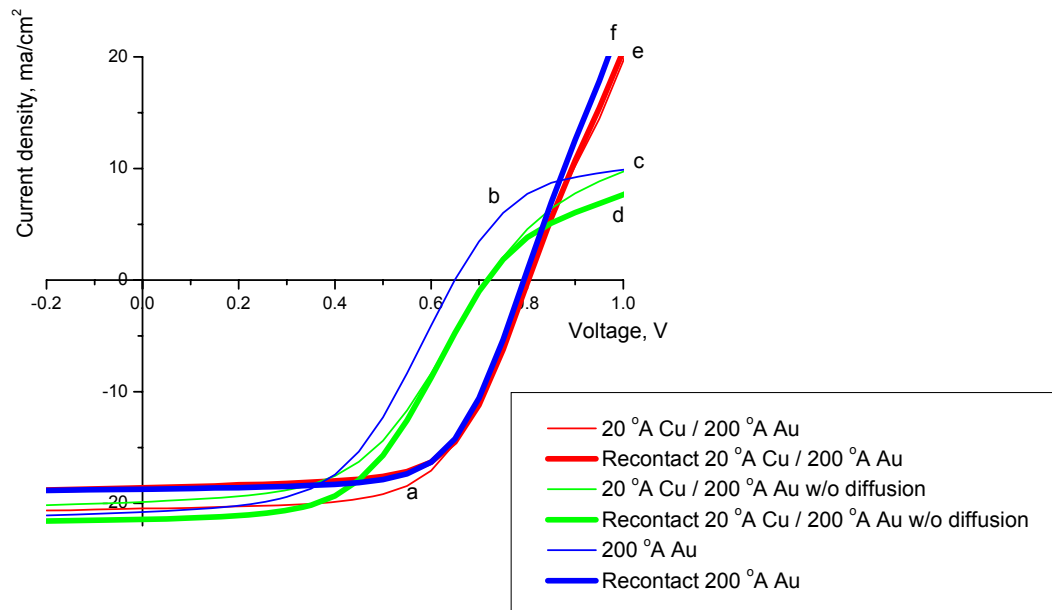


Figure 6. Typical J-V characteristics for the cells with different back contact structures. Letters correspond to the cases discussed in the text.

Figure 7 supports these observations from individual cell J-V curves in the form of statistics from first and second level metrics—efficiency, V_{OC} , J_{SC} , and FF.

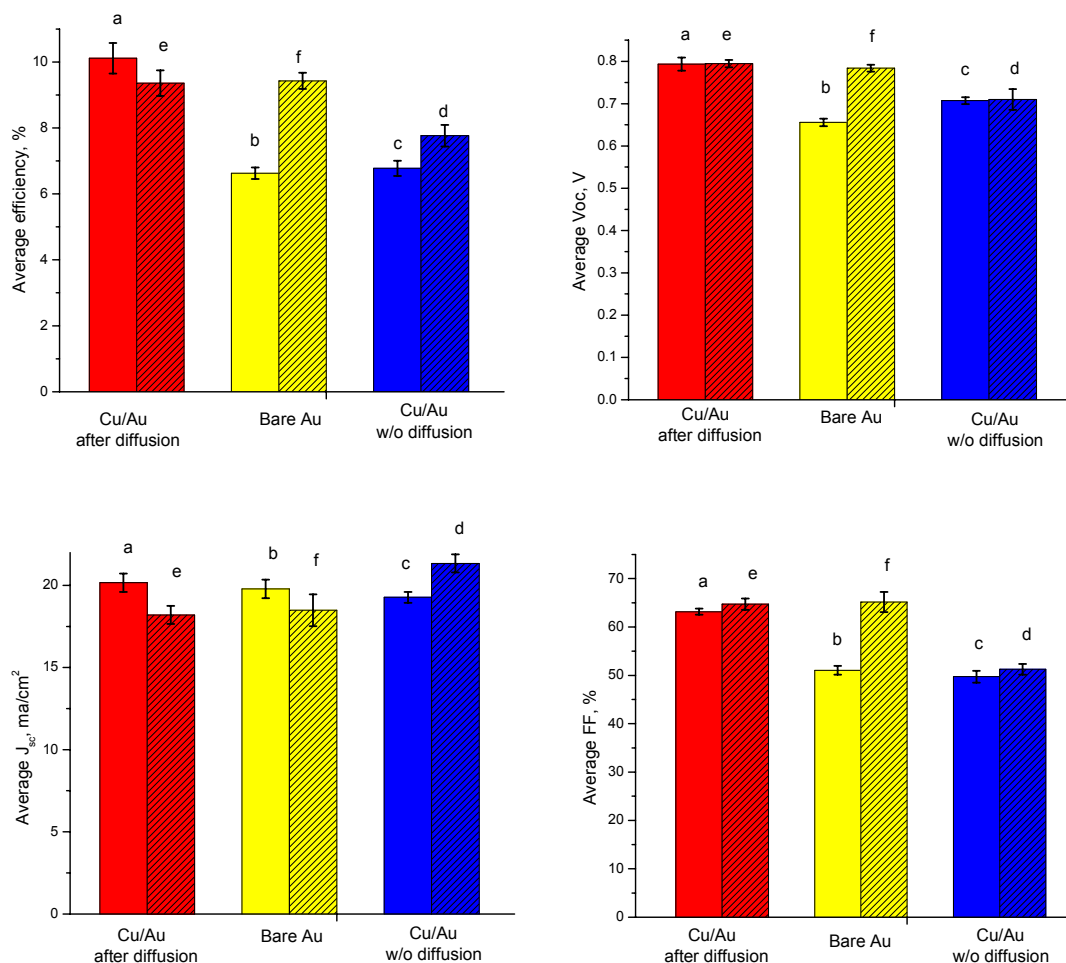


Figure 7. J-V parameters for cell with different back contacts. Solid colors represent regular cells and crossed ones are cells with that were “recontacted.” Letters on top correspond to the letters of Figure 6 and have explanation in the text.

Conclusion

It was first observed by Cu K-alpha fluorescence as a part of our EXAFS study of UT cells that the majority (about 90%) of the Cu remains at the CdTe / BC interface even after thermally activated diffusion and peels away with the Au metal and epoxy. Our recent high-resolution TEM study along with some data from other groups¹ confirm this result. See below. It was also shown later that this Cu is predominantly in an oxidized state. It is still unclear, though, what the effect is of this oxidized Cu at the back contact interface. It does not appear to be active in forming a p+ type region at the back contact. This study shows that although removing the interfacial oxide layer does lower average cell performance, the net result is better than could be expected, especially taking into account that implemented “peel-off” technique allows one to reduce the net amount of Cu in the cell by a factor of 10.

2. High Resolution Transmission Electron Microscopy on Back Contact Region

Collaborations with Jeff Terry and the MRCAT beamline of the Advanced Photon Source in Argonne National Lab, the UT CdTe PV group has studied aspects of the Cu K-edge EXAFS spectrum revealing the local structure of Cu atoms in CdTe solar cells. We have identified the Cu₂O bonding structure in CdCl₂ treated films.² However, the x-ray beam in the photon energy range (from 8.8 keV through 10 keV) penetrates completely through the 2μm CdTe cell structure and leaves questions about the location of the Cu₂O phase in the cell unresolved.

As we reported in Phase I (Deliverable D.1.3), x-ray fluorescence data from peeled off metal back contact layers and the remaining structures of the cells indicate 90% of the 3.5nm evaporated Cu remains in the Cu/Au back contact structure. This indicates that very little copper diffuses into CdTe after the 45 minute heating at 150 °C.

A high resolution investigation into the Cu distribution in the region near the Au back contact was needed to provide better evidence of the Cu location. Such study requires nanometer scale resolution, since the evaporated Cu layer is only 3.5 nm. To obtain direct evidence of the interfacial Cu₂O structure, we have used High Resolution Transmission Microscopy (HRTEM), which can provide Z-contrast imaging with point-to-point resolution of 1.7 Å together with X-ray energy dispersive spectroscopy (EDS).

Since early 2006, we have collaborated with Kai Sun and the Electron Microbeam Analysis Laboratory (EMAL) at the University of Michigan working on HRTEM of our rf sputtered samples. We used a JEOL 3011 ultra-high resolution microscope (~0.17nm) and a JEOL 2010F analytical electron microscope that can be operated either in TEM or STEM mode (~0.17 nm). Sample preparation was done mostly at the University of Toledo with final ion beam thinning at UMich using a Gatan 691 Precision Ion Polishing System (PIPSTM).

Figure 8 shows the high resolution cross sectional image of the back contact region of sputtered CdTe cells, collected in transmission mode. The micrograph clearly shows the lattice structure of CdTe and Au. The most important feature that the HRTEM image demonstrates is a continuous interfacial layer with thickness of approximately 4 Å which is observed everywhere along the interface between CdTe and Au. This interfacial layer appears as the thin layer between CdTe and Au brighter than the other two in the image of Figure 8. Lower Z number elements in this layer produce stronger electron beam intensity collected in transmission through the material. The contrast of the images indicates this interfacial layer between CdTe/Au contains an element with Z number lower than Cd, Te and Au, which we believe is most likely copper. We are continuing our work on fine-probe EDS spectra from the interfacial layer with the electron beam focal spot size 4Å or less and the ones from CdTe and Au to confirm the high copper concentration at CdTe/Au interface.

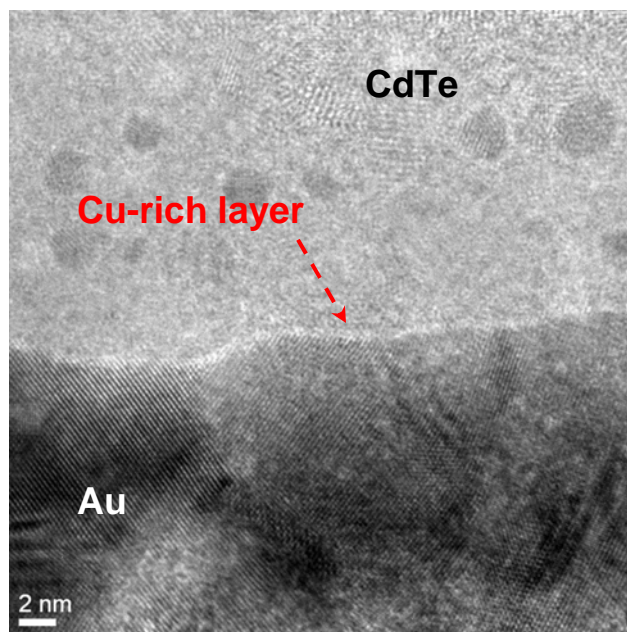


Figure 8 High resolution TEM image with point-to-point resolution 1.7 \AA at the CdTe/Au interface.

3. Cu K-edge EXAFS of Complete CdTe Devices

a. Introduction

We have been working on Cu K-edge EXAFS to determine the local structure of the majority of Cu in CdTe based solar cells. Most of the diffused copper has been found to bind with oxygen in the form of Cu_2O in CdCl_2 treated CdTe films. However, in the film without chloride treatment, copper was found to bind with tellurium in a similar structure, Cu_2Te . We have also studied EXAFS of Cu in CdS polycrystalline films diffused with copper. The results indicate strong scattering from sulfur neighbors (as a Cu-S scattering path in Cu_2S), as reported in the annual technical report for phase I (Deliverable D.1.7). All these studies were done on CdTe or CdS films deposited on high purity fused silica to avoid any possible signal contamination from heavy elements in regular TEC glass, such as Cu or Zn impurities. No spectra from devices with the completed structure (soda-line glass/TCO/CdS/CdTe/metal contact) have been investigated.

In order to study the local structural change of copper in completed CdTe cells, we prepared sputter-deposited CdS and CdTe layers on fused silica substrates. With this structure, a built-in field at the p-n junction is established similar to a completed solar cell but without x-ray fluorescence contamination from TCO-coated soda-lime glass. Doped ZnO as front contact would also be problematic for this study, because the photon energy of the Zn K_α fluorescence signal at 8639 eV is close to the one of Cu K_α (8048 eV) and has been observed before affecting the detection capability of the high purity Ge detector at MRCAT beamline in APS.

In Phase 1 (Deliverable D.1.3), we reported our work on the Cu K-edge EXAFS from complete CdTe solar cell structures. A strong peak arising from the Cu-O bond in the $\chi(R)$ spectrum was observed. However, there were two other peaks at around 2 \AA and 2.74 \AA which

were undetermined at that time partly for lack of spectra from reference structures. Following our x-ray fluorescence study of peeled-off Au contact layers (Deliverable D.1.3) and our recontact study (See Section 1 in this report.), we hypothesized that these two peaks are from a Cu-Au alloy structure. And this hypothesis was later confirmed by our High Resolution Transmission Electron Microscopy images (see section 2 in this report) and EDS (to be reported in the future).

Here we are reporting our experimental and modeling effort on the Cu K-edge EXAFS study of as-grown, complete CdTe cells.

b. Sample preparation

In this study, we prepared standard cells on TEC 7 glass and CdS/CdTe/metal contact structures with the same thickness on fused silica. The thicknesses of CdS and CdTe are 0.13 and 2.3 μm , respectively. Deposition was carried out in 18 mTorr Ar at a substrate temperature of 250 $^{\circ}\text{C}$ without vacuum break between the n-type and p-type layers deposition. Film growths on the two different substrates were finished in separate but consecutive depositions, instead of side-by-side deposition, because of different emissivity of the two substrates. And as the next step, standard vapor CdCl_2 treatment was carried out and followed with evaporation of 35 \AA Cu and 200 \AA Au. The whole process was finished with 45 minutes of heating in ambient air at 150 $^{\circ}\text{C}$ as back-contact activation. Besides the CdS and CdTe deposition, all the following processes were carried out on the two types of samples (on TEC 7 and fused silica) side by side. EXAFS data were collected from the CdS/CdTe/Cu/Au samples on fused silica and the corresponding J-V data were measured on the complete sister cells on TEC 7, which had 11.4% efficiency.

c. Cu_2O and Cu-Au alloy in Complete Cell Structure

After data extraction, the modulus of the phase-uncorrected radial distribution function, $|\chi(\text{R})|$, of the as-grown sample is plotted in Figure 9a. For comparison, the spectrum of Cu_2O reference is also plotted. The major peak at 1.47 \AA arises from the first nearest neighbor of oxygen atoms as in the Cu_2O structure. Even though the peak width is different from the one of Cu_2O , the real and imaginary parts of $\chi(\text{R})$ function (Figure 9b and c) indicate it is due to scattering intensity contributions from the other two peaks at 2 \AA and 2.73 \AA .

Copper is a fast diffuser in CdTe crystals, and diffuses even faster along grain boundaries. In the complete cell structure, copper may accumulate in the CdS layer via the diffusion from back contact through CdTe during the last back contact activation process. Therefore the sulfur neighbors may be considered as the scattering origin of one of the two peaks at 2 \AA and 2.73 \AA . However, by comparing the imaginary and real parts of the $\chi(\text{R})$ functions, neither of the two peaks is found to be generated by scattering from sulfur neighbors (as the Cu-S scattering path, which has been observed in single CdS film).

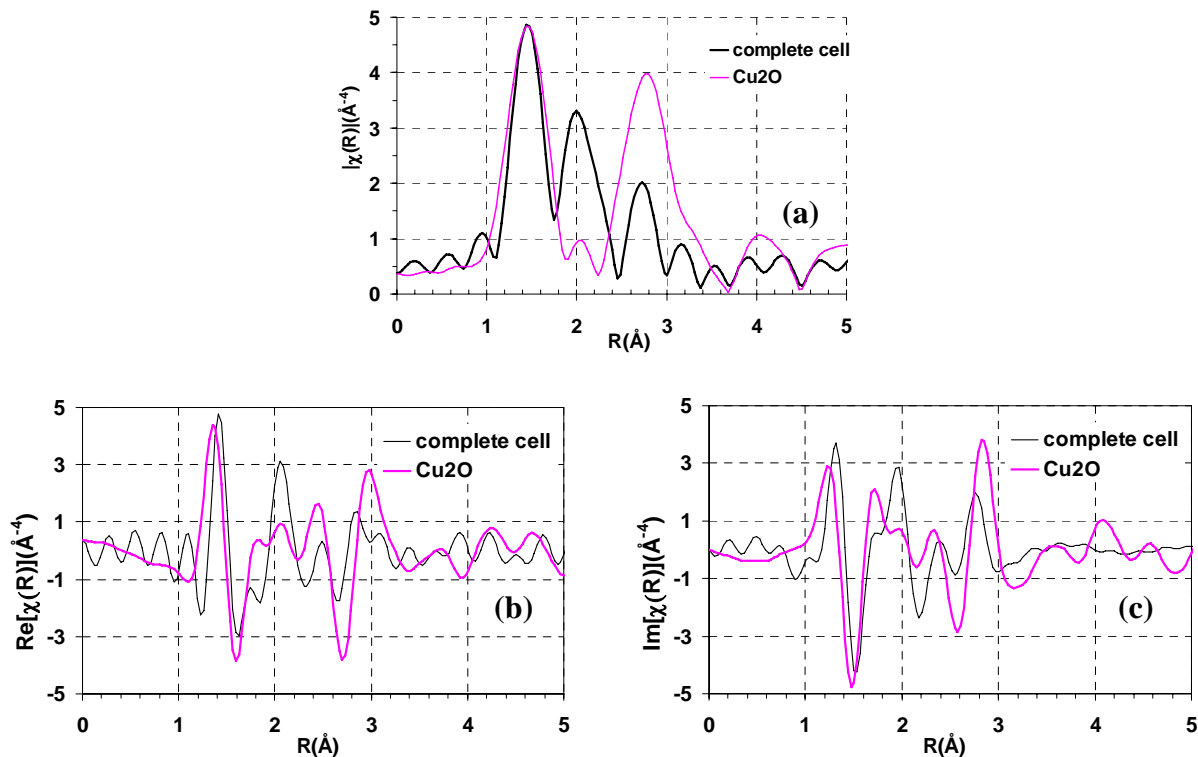


Figure 9 $\chi(R)$ functions of sample with complete cell structure and Cu_2O reference.

The two peaks at 2 Å and 2.73 Å are neither generated due to the scattering by tellurium (as in Cu_2Te), nor chlorine (as in CuCl or CuCl_2), nor copper (as in Cu crystal) neighbors. But given the small amount of Cu in the sample, we cannot conclude that Cu_2S and Cu_2Te are not present in the cell. What appear in the EXAFS spectra are the dominant chemical phases of the majority of copper in the samples. Cu_2S and Cu_2Te scattering could be obscured by the signatures of Cu_2O and the other chemical phases.

The theoretical fitting to the two peaks was suggested by our x-ray fluorescence study of peeled off Au contact layer, the recontact study and the HRTEM images. Scattering paths of Cu-Au and Cu-Cu from a model structure of Cu-Au alloy³ are fitted to the spectrum together with the Cu-O path from Cu_2O reference. The model structure of Cu-Au alloy is a distorted FCC structure with space group $P4/mmm$ and lattice constants: $a = b = 3.966$ Å, $c = 3.673$ Å. In this structure, the first nearest neighbor shell around Cu is eight Au atoms at distance 2.70 Å and the 2nd nearest one is four Cu atoms at 2.80 Å. However, our fitting gives the Cu-Au and Cu-Cu path lengths 2.59 Å and 2.63 Å, respectively (Table 1). The coordination number of the Au and Cu neighbor shell provided in the theoretical fitting is 11.9 and 0.9 respectively. This may suggest that the Cu atom in the Au layer is substituting for the Au atom site in the FCC gold crystal structure, in which there are 12 Au neighbor atoms at 2.88 Å around the Cu atom.

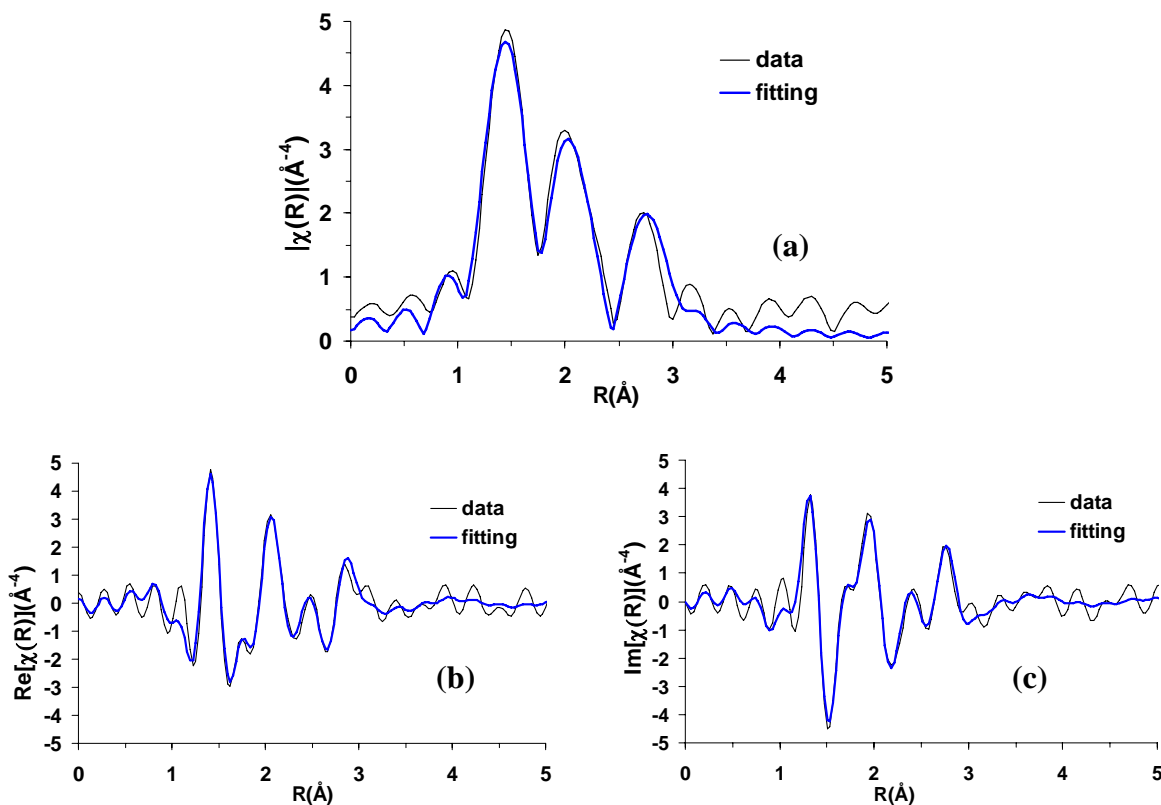


Figure 10 $\chi(R)$ of the complete cell structure (fine lines) and theoretical fitting (thick lines) in the range between 1.2 Å and 3.0 Å. They are compared in modules (a), real part (b) and imaginary part (c).

Table 1 Theoretical fitting parameters of EXAFS from completed cell structure.

bond scattering	N	ΔN (+/-)	R(Å)	$\Delta R(\pm)$	σ^2 (10 ⁻³ Å)	$\Delta\sigma^2(\pm 10^{-3}\text{Å})$	ΔE_o
complete structure							
Cu - O (Cu ₂ O)	1.4	0.3	1.84	0.02	2	fixed	-3.07±4.09
Cu - Au (CuAu)	11.9	3.0	2.59	0.06	21	8	
Cu - Cu (CuAu)	0.9	0.22	2.63	0.11	12	13	
Cu ₂ O							
Cu - O (Cu ₂ O)	1.5	0.39	1.84	0.004	1.6	0.9	8.31±0.32
Cu - Cu (Cu ₂ O)	20.1	5.12	3.04	0.01	27.6	1.5	

An possible explanation for the disagreement with standard Cu-Au bond lengths might be that the amount of copper diffused into the Au layer is too small to form a uniform Cu-Au alloy film. Instead of forming a good Cu-Au alloy, the copper atoms may locate at the grain

boundaries of the polycrystalline Au layer. Lattice dislocation of Au can be clearly seen in the HRTEM image as shown in Figure 8.

d. Conclusion

This EXAFS study of a carefully design sample with a structure close very close to that of a functional cell structure confirms the existence of copper oxide in CdTe solar cell. However, we also find evidence that a major phase of copper in the cell structure is in the form of a Cu-Au alloy.

We are currently using fine-probe EDS spectra on the back contact region collected together with the HRTEM images to confirm the distribution of copper in the gold contact layer. Meanwhile, we are analyzing EXAFS spectra taken on cell structures that have been light-soaked.

Reference:

¹ Yanfa Yan, Kim Jones, Jie Zhou, Xuanzhi Wu and Mowafak Al-Jassim. TEM study of Locations of Cu in CdTe Solar Cells. Mater. Res. Soc. Symp. Proc. Vol. 1012

² Xiangxin Liu, Alvin D. Compaan and, Jeff Terry, "Cu K-edge X-ray fine structure changes in CdTe with CdCl₂ processing", 2004 European MRS meeting, Strasbourg, *Thin Solid Films* **480-481** (2005), pp. 95-98.

³ "Pearson's Handbook of Crystallographic Data for Intermetallic Phases", P. Villars and L.D. Calvert V. 2, Metals Park, Oh : American Society for Metals, 1985.